



Designation: D8351 – 22

Standard Test Method for Determination of Trace Elements in Biodiesel and Biodiesel Blends by Microwave Plasma Atomic Emission Spectrometry (MP-AES)¹

This standard is issued under the fixed designation D8351; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the determination of elements in biodiesel and biodiesel blends by microwave plasma atomic emission spectrometry (MP-AES). The specific elements within the scope of this method are calcium (Ca), magnesium (Mg), phosphorus (P), potassium (K), and sodium (Na).

1.2 This test method conforms to Practice D6300, subsection 8.4.5, valid test result range, and subsection 8.4.6, working range specifications. The valid test result range and working range are recent additions to Practice D6300, and a graphical representation using example values is shown in Appendix X2, Test Method Operating Range.

1.3 Method working range:

high expected concentration limit = highest ILS sample mean
low expected concentration limit = lowest ILS sample mean if:
lowest ILS sample mean $- R_{\text{lowest ILS sample mean}} > 0$; otherwise it is determined by solving for X using the following equation:
 $X - R_x = \text{coarsest resolution, determined by } 0.5 \cdot \sigma_{r, \text{lowest ILS sample mean}}$

Biodiesel and Biodiesel Blends

Element	Method Working Range (expected mg/kg)
Calcium	0.24 to 15.01
Magnesium	0.12 to 11.55
Phosphorus	1.69 to 14.24
Potassium	0.49 to 13.98
Sodium	0.90 to 14.30

1.4 This test method uses organic elemental standards in organic solvents for calibration and does not purport to quantitatively determine insoluble particulates. Analytical results are particle size dependent, and particles larger than a few micrometers can cause results to appear low.

1.5 Elements present at mass fractions above the upper limit of the calibration curves can be determined with additional appropriate dilutions. Elements shall be measured at the wavelengths presented in Table 1. Alternate wavelengths noted in Appendix X1 may be used in the rare case of spectral interference.

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.03 on Elemental Analysis.

Current edition approved May 1, 2022. Published June 2022. DOI: 10.1520/D8351-22.

1.6 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.7 This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.

1.8 This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

2. Referenced Documents

2.1 ASTM Standards:²

- D4057 Practice for Manual Sampling of Petroleum and Petroleum Products
- D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products
- D4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards
- D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance
- D6300 Practice for Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products, Liquid Fuels, and Lubricants
- D6792 Practice for Quality Management Systems in Petroleum Products, Liquid Fuels, and Lubricants Testing Laboratories
- D7372 Guide for Analysis and Interpretation of Proficiency Test Program Results

² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For Annual Book of ASTM Standards volume information, refer to the standard's Document Summary page on the ASTM website.

2.2 ISO Standards:³

ISO 8573-1 Compressed air – Part 1: Contaminants and purity classes

3. Terminology

3.1 Definitions:

3.1.1 *biodiesel*, *n*—fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, designated B100.

3.1.2 *biodiesel blend (BXX)*, *n*—a homogeneous mixture of hydrocarbon oils and mono-alkyl esters of long chain fatty acids.

3.1.2.1 *Discussion*—In the abbreviation BXX, the XX represents the volume percentage of biodiesel fuel in the blend.

3.1.2.2 *Discussion*—Diesel fuel, fuel oil, and non-aviation turbine oil are examples of hydrocarbon oils.

3.1.3 *biodiesel fuel*, *n*—synonym for biodiesel.

3.1.4 *calibration*, *n*—process by which the relationship between signal intensity and the elemental mass fraction is determined for a specific element analysis.

3.1.5 *emission spectroscopy*, *n*—measurement of energy spectrum emitted by or from an object under some form of energetic stimulation; for example, light, electrical discharge, and so forth.

3.1.6 *quality control sample*, *n*—for use in quality assurance program to determine and monitor the precision and stability of a measurement system; a stable and homogenous material having physical or chemical properties, or both, similar to those of typical samples tested by the analytical measurement system.

3.1.6.1 *Discussion*—This material should be properly stored to ensure sample integrity, and is available in sufficient quantity for repeated long term testing.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *calibration curve*, *n*—plot of signal intensity ratios versus elemental mass fraction using data obtained by making measurements with standards.

3.2.2 *continuing calibration blank (CCB)*, *n*—a blank calibration standard that does not contain any elements of interest, analyzed immediately following each CCV; this solution is the biodiesel blank.

3.2.3 *continuing calibration verification (CCV)*, *n*—a mid-range calibration standard analyzed after every ten sample analyses to verify that the instrument calibration has not drifted.

3.2.4 *diluted stock standard (DSS)*, *n*—a material prepared by gravimetric dilution of stock standard (OSS) to facilitate preparation of working standards.

3.2.5 *high solids nebulizer*, *n*—a device that generates an aerosol by flowing a liquid over a surface that contains an orifice from which gas flows at a high velocity.

3.2.6 *internal standard (IS)*, *n*—an element not present in the sample which is added to each solution, calibration blank, working standards, and samples and used to calculate quantitatively the element of interest.

3.2.7 *microwave plasma (MP)*, *n*—a high-temperature microwave plasma is created by coupling the magnetic field of the microwave energy into the plasma.

3.2.8 *organometallic stock standard (OSS)*, *n*—a material which is well characterized for the elements of interest, with assigned mass fraction values traceable to the SI.

3.2.9 *working standard (WS)*, *n*—a material prepared from dilution of the DSS organometallic standard containing the elements of interest for the purpose of quantitative calibration.

4. Summary of Test Method

4.1 For determination of elements (Ca, Mg, K, Na, and P) in biodiesel and biodiesel blends, samples are introduced through the nebulizer and spray chamber into the microwave plasma atomic emission spectrometer. An internal standard (IS) is incorporated and the emission intensity of each element is divided by the emission intensity of the IS to produce an adjusted intensity for each element. Calibration standards are prepared by diluting organo-elemental standards in narrow cut kerosene solvent and measured with the IS in the same way as the samples. Quantitative results are obtained by comparing the intensity ratios measured from the samples to the intensity ratios obtained from the calibration standards.

5. Significance and Use

5.1 This test method covers the determination of five elements (Ca, Mg, K, Na, and P) in biodiesel and biodiesel blends.

5.2 The presence of metals and metalloids in engine fuels can influence the performance of engines and contribute to shortening the lifetime of the equipment. In addition, some elements act as catalyst poison contributing to increases in the amount of unwanted gases and particulate matter emitted by vehicles.

6. Interferences

6.1 *Spectral*—Check all spectral interferences expected from the elements listed in Table 1 using manufacturer’s operating guide to develop and apply correction factors to compensate for the interferences. To apply interference

TABLE 1 Element Wavelengths

NOTE 1—These wavelengths shall be used for this method. The precision of this method is based on these wavelengths.

Element	Wavelength (nm)	Standards Used in each Curve (mg/kg)
Calcium	396.847	Biodiesel Blank, 0.1, 1, 5, 10
Magnesium	285.213	Biodiesel Blank, 0.1, 1, 5, 10, 20
Phosphorus	213.618	Biodiesel Blank, 1, 5, 10, 20
Potassium	766.491	Biodiesel Blank, 0.1, 1, 5, 10, 20
Sodium	588.995	Biodiesel Blank, 0.1, 1, 5, 10, 20
Yttrium (IS)	371.029	20 mg/kg (dilution to 10 mg/kg during Tee assembly aspiration with the sample specimen.)

³ Available from International Organization for Standardization (ISO), ISO Central Secretariat, Chemin de Blandinnet 8, CP 401, 1214 Vernier, Geneva, Switzerland, <https://www.iso.org>.

corrections, all mass fractions must be within the linear response range of each element listed in [Table 1](#).

6.1.1 Spectral interferences can usually be avoided by using the specified wavelengths in [Table 1](#). Guidance on spectral interference is in [Appendix X1](#). Interference from copper may affect the phosphorous measurement, refer to [Appendix X2](#).

6.2 *Particulates*—Particulates can clog the nebulizer thereby causing erroneous results.

7. Apparatus

7.1 *Balance*, top loading or analytical, with automatic tare, that measures to at least 0.0001 g and with sufficient capacity to weigh prepared solutions.

7.2 *Microwave Plasma Atomic Emission Spectrometer*⁴—MP-AES—A sequential, emission based multi-element analytical technique that uses a microwave-induced plasma for sample excitation. The operating software provides programmed sequential sample operation and quantitative data processing. A torch and microwave generator are used to form a sustained plasma that can be used for making measurements at the specified wavelengths.

7.2.1 *Sample Introduction System*—The sample introduction system shall be composed of solvent-resistant tubing, a double-pass cyclonic chamber, and an inert high solids nebulizer. The nebulizer must provide a homogeneous aerosol, comprised of small droplets with a narrow distribution of droplet sizes.

7.2.2 *Gas Control System*—All gas flows shall be controlled by automated flow control devices.

7.2.3 *Instrument Control Software for Background Correction*—Spectrum correction software which allows for manual or automated background correction. Software optimizes nebulizer flow at each wavelength. Introduction conditions and settings are presented in [Table 2](#). Instrument operating conditions for elemental determination in biodiesel samples are presented in [Table 3](#).

⁴The sole source of supply of the Microwave Plasma Atomic Emission equipment, OneNeb Series 2 and instrumentation known to the Committee at this time is Agilent Technologies, Inc., 5301 Stevens Creek Blvd., Santa Clara, CA 95051. Agilent Technologies also has authorized sales and service organizations in selected geographical areas. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee which you may attend.

TABLE 2 Sample Introduction Conditions for Elemental Determination in Biodiesel Samples

Instrument Parameter	Operating Condition
Nebulizer	Inert High Solids nebulizer (such as OneNeb Series 2 nebulizer).
Spray chamber	Cyclonic double-pass.
Sample tubing	Fluoroelastomer tubing can be used for this test method. Other suitable tubing may be used and must be evaluated by the user. (0.38 mm ID). Internal standard and sample tubing for teeing is orange/green (0.38 mm ID) which provides a 1:1 ratio.
Waste tubing	Fluoroelastomer Blue/blue 1.65 mm ID.

TABLE 3 Instrument Operating Conditions for Elemental Determination in Biodiesel Samples

Instrument Conditions	MP-AES
Pump rate	5 rpm
Read time	3 to 10 s (to be determined experimentally in each lab)
Number of replicates	3
Sample uptake delay	Approximately 60 s (depends on lab set-up, tubing configuration and tubing length to be determined experimentally)
Stabilization delay	Approximately 30 s (depends on lab set-up, tubing configuration and tubing length to be determined experimentally)
Background correction	Auto
Air injection required	Yes

7.3 *Peristaltic Pump*—A peristaltic pump is required for sample introduction. The precision of this test method (Section [17](#)) was determined using 5 rpm.

7.4 *Test Specimen Containers*, of appropriate size, glass or PTFE vials or bottles, with screw caps. Containers of other suitable materials may be used but the user must evaluate them for use.

7.5 *Dispensing vessel*, provides a consistent means for dispensing of solutions more easily for gravimetric measurements; a pipette, volumetric dispenser, or similar device which is used to add consistent quantities of internal standard to samples and calibration standards, etc.

7.6 *Internal Standard Peristaltic Tee Assembly*—Any tee-type fitting composed of solvent resistant material used to facilitate the simultaneous addition of the internal standard and sample directly into the nebulizer.

8. Reagents and Materials

8.1 *Purity of Reagents*—Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.⁵

8.2 *Organometallic Standards in Organic Matrix*—Commercial multi-element or mono-element stock solutions may be purchased and prepared according to Practice [D4307](#).

8.3 *Biodiesel Blank*—This fluid is intended for use as a calibration blank solution or diluent for the analysis of elements in biodiesel products. This fluid is also used as the Continuing Calibration Blank (CCB). The solvent is considered acceptable for use under the condition where the solvent elemental (elements of interest) intensity response is equal to or less than 25 % compared to the intensity response of the lowest calibration point.

8.4 *Nitrogen*—High purity from a compressed gas cylinder or nitrogen generator. Working pressure is 450 kPa to 600 kPa (65 psi to 87 psi).

⁵ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

8.4.1 *Plasma Support Gas*, 99.5 % purity nitrogen containing <0.5 % oxygen and <4 ppm water vapor, supply at 25 L/min.

8.5 *Air*—Air supply, as follows:

8.5.1 *Specification*—ISO 8573-1:2010 Class 1.4.3, recommended pressure 500 kPa.

8.5.2 *Pre-Optics-Purge (POP) Gas*—Supply at 25 L/min.

8.5.3 *Monochromator Optics Purge*, 10 L/min.

8.5.4 *Plasma Air Addition*, for organic analysis 1.5 L/min.

8.6 *Argon*—Purity as specified by supplier specifications, supply at 0.5 L/min is only required during plasma ignition. After the initial formation of argon plasma, the gas supply is switched to nitrogen used during the test operation.

8.7 *Peristaltic Pump Tubing*, (Solva or Viton)—The pump tubing must be able to withstand at least 6 h exposure to the dilution biodiesel and dilution solvent. Either Solva and Viton tubing can be used. Inspect the peristaltic pump tubing daily and replace deteriorating tubing. Solvent resistant tubing such as fluoroelastomer or other materials can be used but were not used in the ILS. The user must evaluate alternate tubing material, accordingly.

8.8 *Organic Solvents*—Narrow-cut kerosene is used when making the IS solution. The solvent is considered acceptable for use under the condition where the solvent elemental (elements of interest) intensity response is equal to or less than 25 % compared to the intensity response of the lowest calibration point.

8.9 *Organometallic Internal Standards in Organic Matrix*—Commercially available internal standard solutions containing oil soluble Yttrium (Y) at known certified concentrations with expanded uncertainty not exceeding 10 % relative uncertainty of the certified mass fraction.

9. Sampling

9.1 *General Requirements*:

9.1.1 Samples to be analyzed by this test method shall be collected using procedures outlined in Practice D4057 or Practice D4177, where appropriate. Do not use “sampling by water displacement.” Biodiesel is more water-absorbent than the hydrocarbon base in a biodiesel blend.

9.1.2 Protect samples from excessive temperatures prior to testing. Do not allow samples to exceed 40 °C.

9.2 *Sample Handling During Analysis*:

9.2.1 When analyzing samples using the MP-AES, the sample temperature shall be within the range of 20 °C to 25 °C.

9.2.2 After analysis, if the sample is to be retained, reseal the container before storing.

9.3 It is extremely important to homogenize samples in the original sample container to obtain a representative test sample. Employ adequate mixing and sampling procedures, especially for heavier samples. If using hand shaking, vigorously shake the sample container for about 30 s immediately prior to taking an aliquot for analysis. Vortex mixers can help in making the samples uniform.

10. Preparation of Apparatus

10.1 *Nitrogen Purge*—Ensure that the gas lines are adequately purged with nitrogen before attempting to ignite the plasma following the manufacturer’s recommended procedure.

10.2 *Instrument MP Excitation Source*—Initiate the plasma source according to manufacturer’s instructions allow at least 30 min warm-up before performing the analysis. During this warm-up period, feed narrow cut kerosene solvent through the sample introduction system. Inspect the torch for carbon buildup during the warm-up period. If carbon buildup occurs, replace the torch immediately and consult the MP-AES Easy Fit Torch manufacturer’s maintenance guide to take proper steps to remedy the situation.

10.3 *Wavelength Calibration*—Prepare the instrument for analysis by performing a wavelength calibration, dark current scan, and torch alignment scan in accordance with manufacturer’s instructions when the method is first run on the MP-AES. Subsequent wavelength calibration, torch alignment and Dark current is typically only necessary once a month or after instrument maintenance.

10.4 *Peristaltic Pump*—Verify the solution uptake rate is set to a peristaltic pump rate of 5 rpm. Before starting analysis each day, inspect the pump tubing and replace if instrument results are not repeatable.

10.5 *Operating Parameters*—Assign the appropriate operating parameters as shown in Table 4, so that the desired elements can be determined. Parameters to be included are element, wavelength, background correction points.

11. Calibration and Standardization

11.1 The linear range must be established for the particular instrument being used. This is accomplished by running a blank and standards. Prepare serial dilutions of working standards (WS) for Ca, Mg, P, K, and Na at final mass fractions of 0.1 mg/kg, 1.0 mg/kg, 5.0 mg/kg, 10.0 mg/kg, and 20.0 mg/kg per element with the biodiesel blank.

11.1.1 Spectral background correction shall be used. When mass fractions are low, background changes, which can result from variability in the compositions of test specimen solutions, can affect the accuracy of the analysis. Background correction minimizes errors due to variable background intensities.

11.2 Establish the calibration curve by using the working standards (WS) to establish the calibration. The acceptable calibration correlation coefficient is 0.995 or greater. If the

TABLE 4 Analyte Nebulizer Flow Rate and Gas Control System Settings

Element	Wavelength (nm)	Viewing Position ^A	Nebulizer Flow (L/min)	Air Injection Flow Rate	Background Correction
Calcium	396.847	0	0.5	High	Auto
Magnesium	285.213	0	0.5	Medium	Auto
Phosphorus	213.618	0	0.5	Medium	Auto
Potassium	766.491	0	0.5	High	Auto
Sodium	588.995	0	0.5	High	Auto
Yttrium (IS)	371.029	0	0.5	High	Auto

^AViewing position of “0” is the center of the central channel of the plasma.

correlation coefficient is less than 0.995 the user shall investigate to determine the source of error or contamination and make corrections before proceeding with testing.

11.3 *Internal Standard (IS)*—The internal standard solution shall contain a mass fraction of yttrium at a concentration of 20 mg/kg in narrow cut kerosene. The internal standard is added to the sample solution by using a tee assembly for continuous addition or by gravimetric addition during sample preparation. An example of continuous addition Tee used in the interlaboratory study for this test method is shown below in Fig. 1. The use of gravimetric addition of the internal standard without the Tee was not used in the interlaboratory study.

12. Preparation of Test Specimens, Standards, and Quality Control (QC) Samples

12.1 *Blank*—Straight Biodiesel Blank. The blank shall be tested on the designated instrument described in this standard. The blank test shall be performed by testing the blank and the lowest calibration point standard using the same instrument conditions designated for subsequent sample testing.

12.2 *Test Specimens*—All biodiesel and biodiesel blend samples shall be tested neat using the same conditions used to test calibration standards and quality control samples.

12.3 *Working Standards*—Prepare working standards by diluting multi-element organometallic standard (OSS) with blank biodiesel to prepare a diluted stock standard (DSS) and working standards with appropriate mass fractions for calibration. Use biodiesel standards straight if they will provide acceptable mass fraction levels for calibration.

12.4 *QC Check Standards*—Prepare a second source QC samples in same organic biodiesel solvent (wt/wt), such that

the concentration is the median of the linear calibration range and 10 % of the top standard. See Practice D6792 for guidance in this area.

13. Quality Control Monitoring

13.1 Confirm the method performance via regular testing of quality control (QC) sample(s) as defined in Practice D6299.

13.2 Record QC sample test results and confirm the statistical control status for the execution of the complete test method using control charts defined in Practice D6299.

13.3 Investigate any out-of-control result for root cause(s). The outcome from this investigation may, but not necessarily, result in instrument re-calibration.

13.4 The frequency of QC testing is dependent on the criticality of the property being measured, the demonstrated stability of the testing process, and business requirements. Generally, a QC sample should be analyzed each testing day with routine samples. The QC frequency should be increased if a large number of samples are routinely analyzed. However, when it is demonstrated that the testing is under statistical control, the QC testing frequency may be reduced. The QC sample testing precision should be periodically checked against the ASTM International published method precision for consistency by Practice D6792.

13.5 The QC material (Practice D6299) that is regularly tested should be representative of the samples routinely analyzed. An ample supply of QC sample material should be available for the intended period of use, and must be homogeneous and stable under the anticipated storage conditions.

13.6 Participation in appropriate proficiency test programs is recommended for monitoring performance relative to industry requirements (Guide D7372).

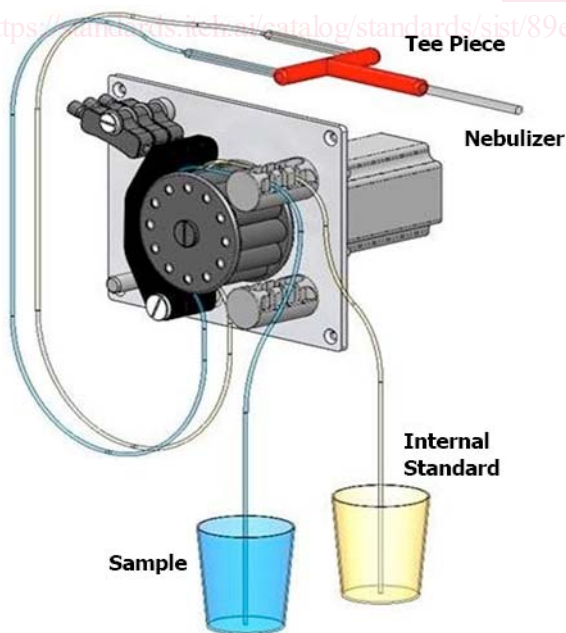
14. Procedure

14.1 *Analysis*—Analyze the test specimen in the same manner as the calibration standards (that is, same integration time, background correction points, plasma conditions, etc.). Analyze all diluted samples as soon as possible or up to or during 24 h after preparation. Allow sufficient rinse time (not less than 60 s) between measurements to avoid memory effects.

14.2 Analyze the Quality Control (QC), Continuing Calibration Blank (CCB), and Continuing Calibration Verification (CCV) standards and unknown samples in the same manner as the calibration standards (that is, same integration time, plasma conditions, and so forth).

14.3 When the measured intensities of the unknown sample test specimen solution exceed the corresponding intensities for the working standard calibration range, either ensure that the calibration curve is linear to the concentration of the element in the test specimen solution or dilute the test specimen solution with the blank solution and reanalyze.

14.4 The CCB and CCV standard shall be analyzed at a frequency of every ten samples during an analytical run. The CCB and CCV standard shall also be analyzed at the beginning of the run, and again after the last analytical sample.



NOTE 1—This figure is for the purpose of providing an example and demonstrating the Tee assembly tubing configuration only. Refer to Section 7 for specific sample container details.

FIG. 1 Internal Standard Solution Tee Assembly